Metal Oxide Nano-Array Catalysts for Low Temperature Diesel Oxidation

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Project ID #: ACE095

Project Overview

Overall objective:

—To develop a unique class of cost-effective and high performance metal oxide based nano-array catalysts for low temperature (at 150 ^{o}C or lower) diesel oxidation

Timeline

- Project start date: 10/01/2014
- Project end date: 12/31/2016
- Percent complete: < 20%

Budget

- Total project funding
  - DOE share: $1,450,000
  - Contractor share: $380,139

Barriers

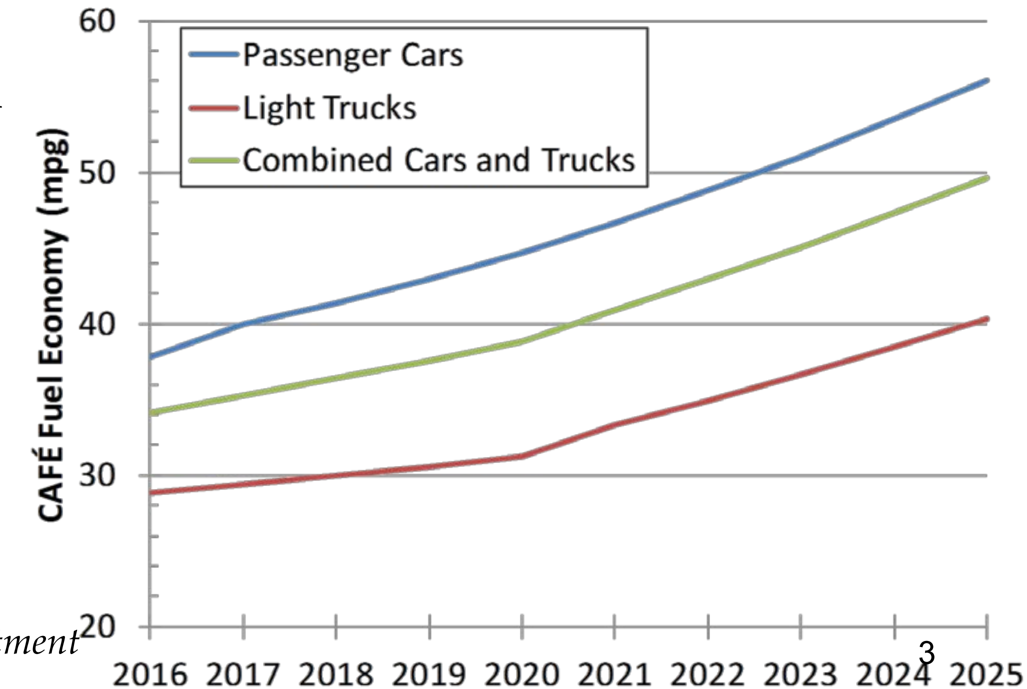
- Barriers addressed
  - Initial Formulation of nano-array catalysts
  - Assembly of nano-array catalysts with reduced usage of metal oxide and noble metals
  - CO and HCs oxidation tests at low temperature

Team Partners

- ORNL, Umicore, and 3D Array Technology LLC

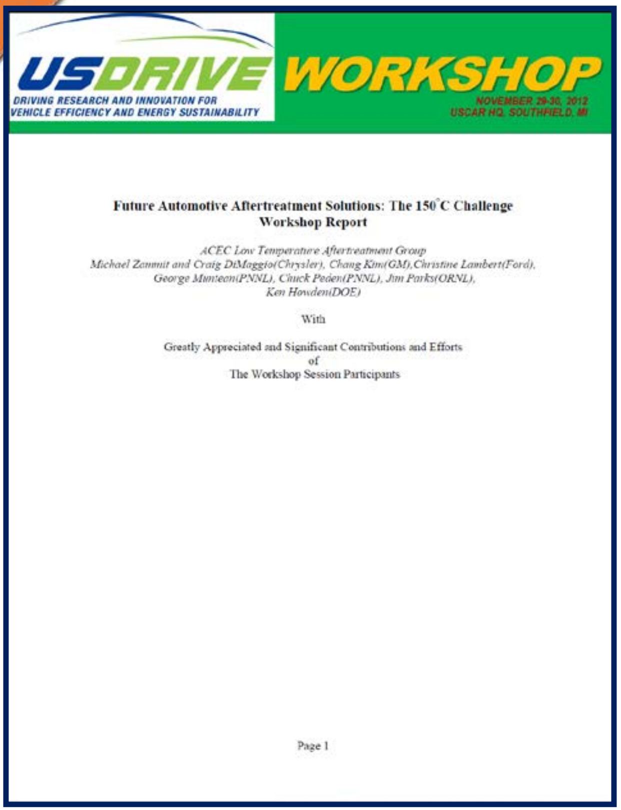
Project Relevance

- Identify and formulate cost-effective and high performance nano-array based catalysts that are compatible to **low temperature combustion engines** with greater fuel efficiency and consequently lower exhaust temperature conditions
- Low temperatures catalysis challenges:
  - Emissions standards harder to meet
  - 10x higher HCs and CO, new chemistry at low temperature, need new DOC.
- Investigate nano-array based catalysts to improve low Temperature catalysis for emission control
  - ~90% conversion at 150°C or lower
- Fuel economy demands



C. DiMaggio, "ACEC Low Temperature Aftertreatment Program", 06/21/2012.

Project Relevance



Future Automotive Aftertreatment Solutions: The 150°C Challenge
Workshop Report

ACEC Low Temperature Aftertreatment Group
Michael Zammit and Craig DiMaggio(Chrysler), Chang Kim(GM),Christine Lambert(Ford), George Muntean(PNNL), Chuck Peden(PNNL), Jim Parks(ORNL), Ken Howden(DOE)

With

Greatly Appreciated and Significant Contributions and Efforts
of
The Workshop Session Participants

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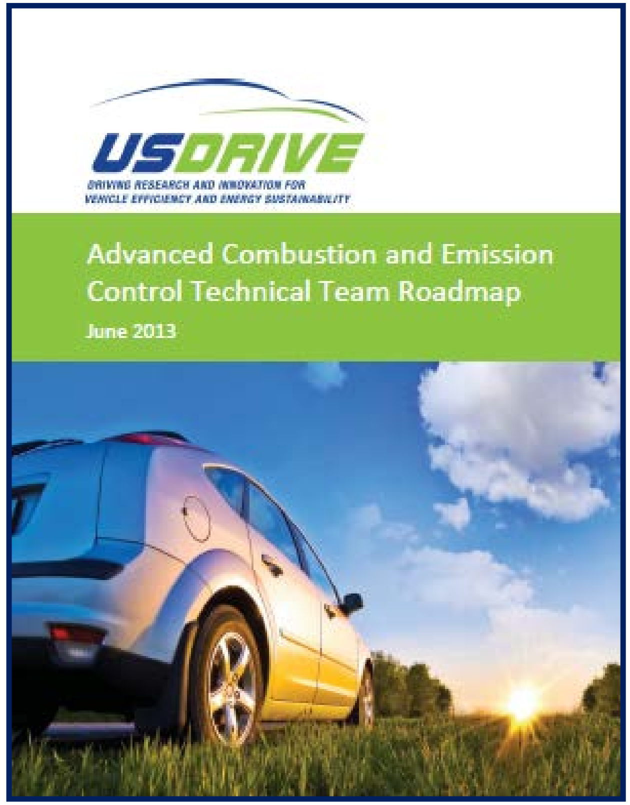
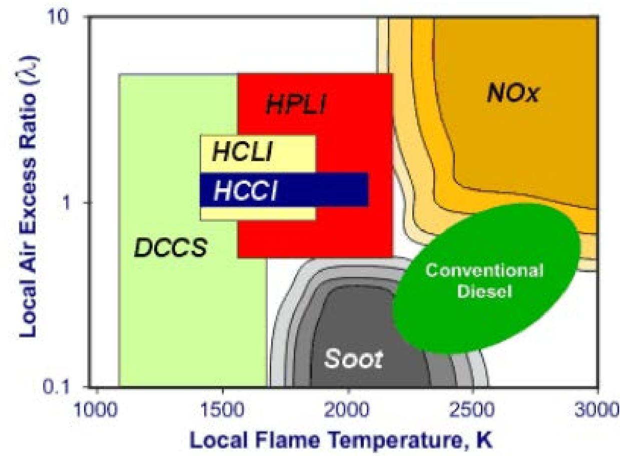
USDRIVE "The 150ºC Challenge" Workshop Report



2013 USDRIVE ACEC Tech Team Roadmap



W. Addy Majewski, Hannu Jääskeläinen, Engine Design for low emission, Dieselnet

Advanced combustion engine technologies:

- Low Temperature Combustion (LTC)
- Dilute Gasoline Combustion
- Clean Diesel Combustion (CDC)

Needs addressed in this project:

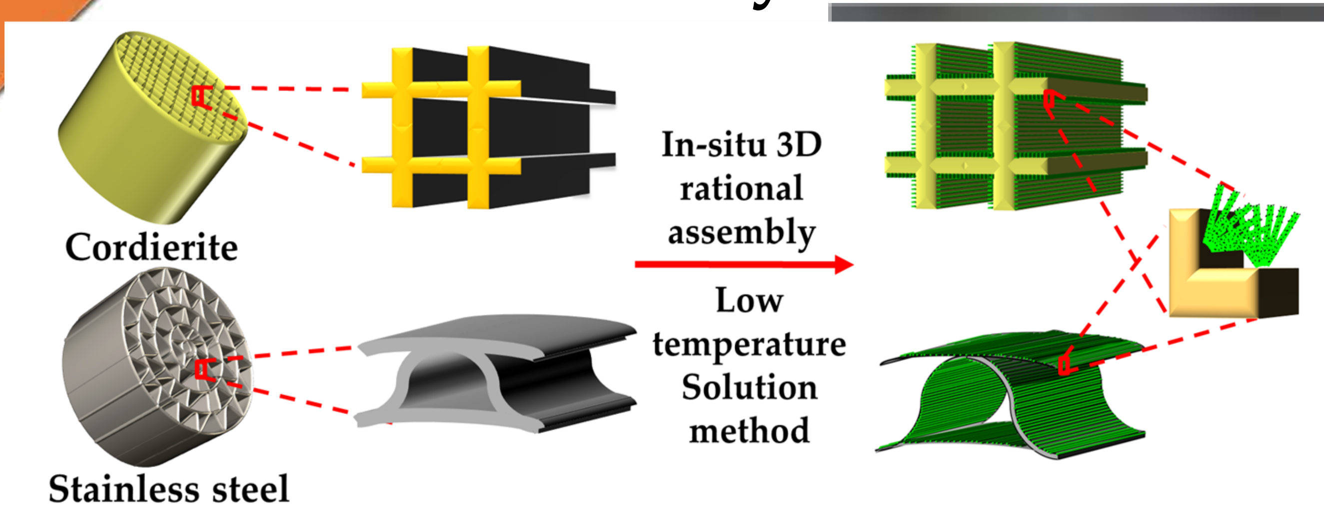
- Lower temperature CO oxidation; HC oxidation; and NO_x reduction
- Reduced PGM
- Better thermal stability

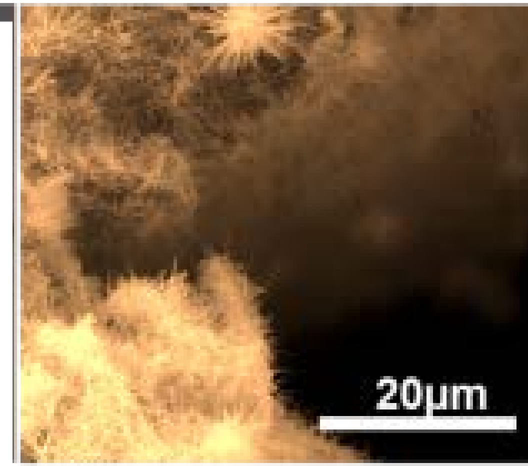
Tasks and Approaches

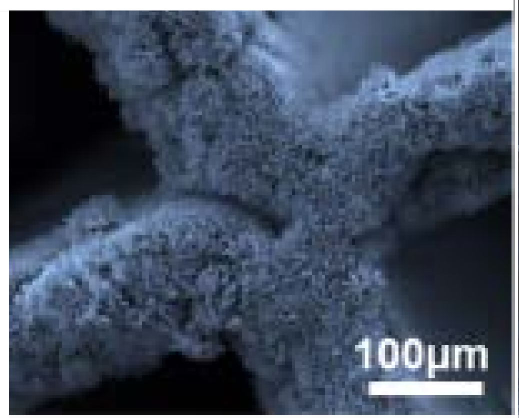
- Tasks in Quarters 1-2, 10/1/2014-3/31/2015
  – Design, assembly and characterization of metal oxide nano-array catalysts
  – Initiation of perovskite and noble metal loading
  – Testing of CO and HCs oxidation over nano-array catalysts

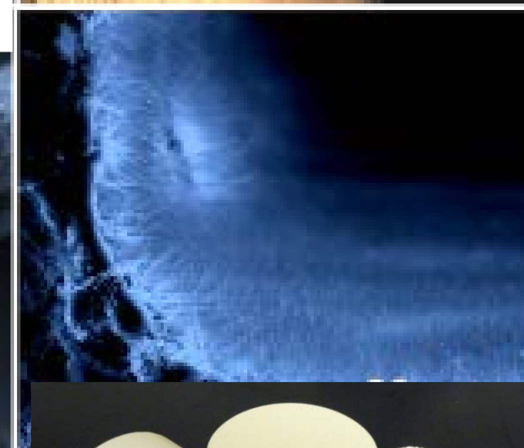
- Approaches:
  - **Synthesis and assembly:**
    Directly grow and assemble 3D metal oxide nano-array catalysts on honeycomb substrates by in-situ solution and gas phase approaches.
  - **Nano-characterization:**
    Investigate the structure, morphology, chemical properties of nano-array catalysts using a range of microscopy and spectroscopy techniques.
  - **Low Temperature Activity, and Stability:**
    Explore the catalytic behavior and stability using benchtop reactors , thermal analysis and temperature programmed analysis tools.

In-situ Growth of Nano-arrays onto Honeycomb Monoliths









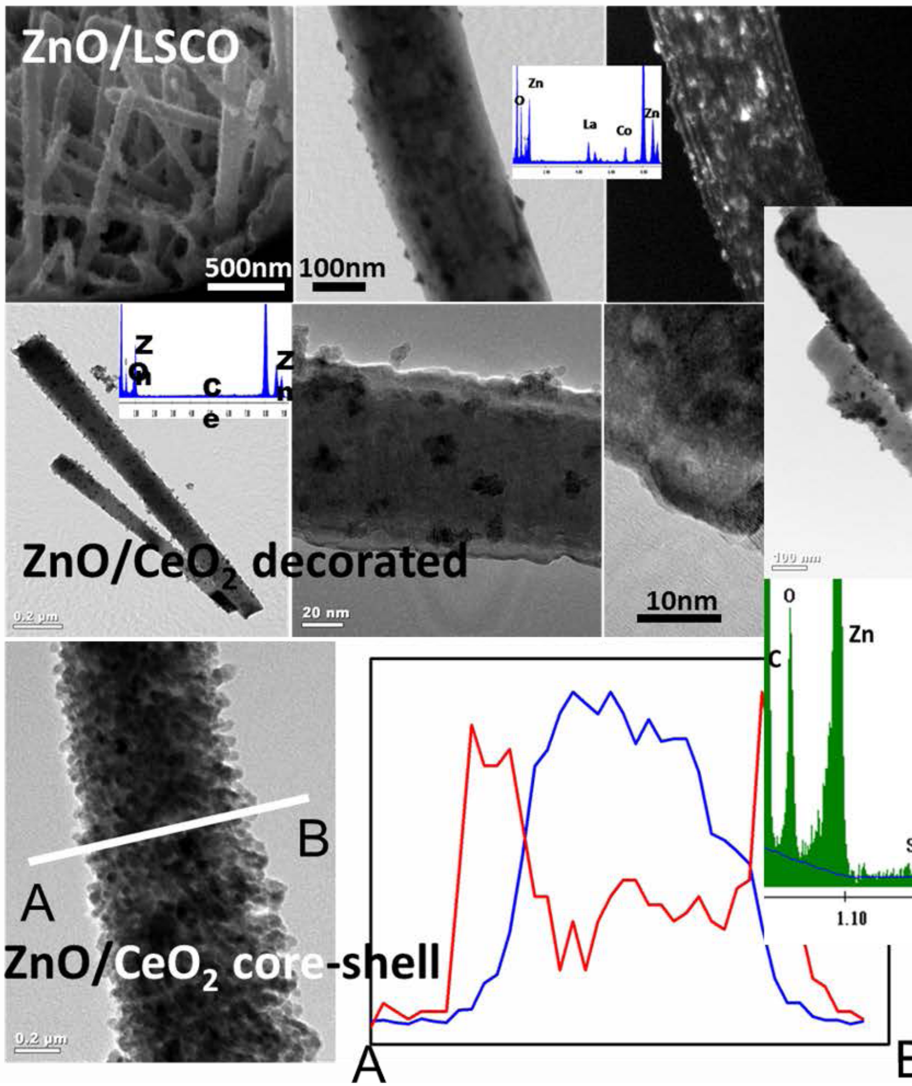
- In-situ growth of nano-array on monolith
- Free of binders, robustness due to the strong substrate-array adhesion after in-situ growth
- Reduced PGM and other materials usage
- Improved efficiency due to size, shape, and structure

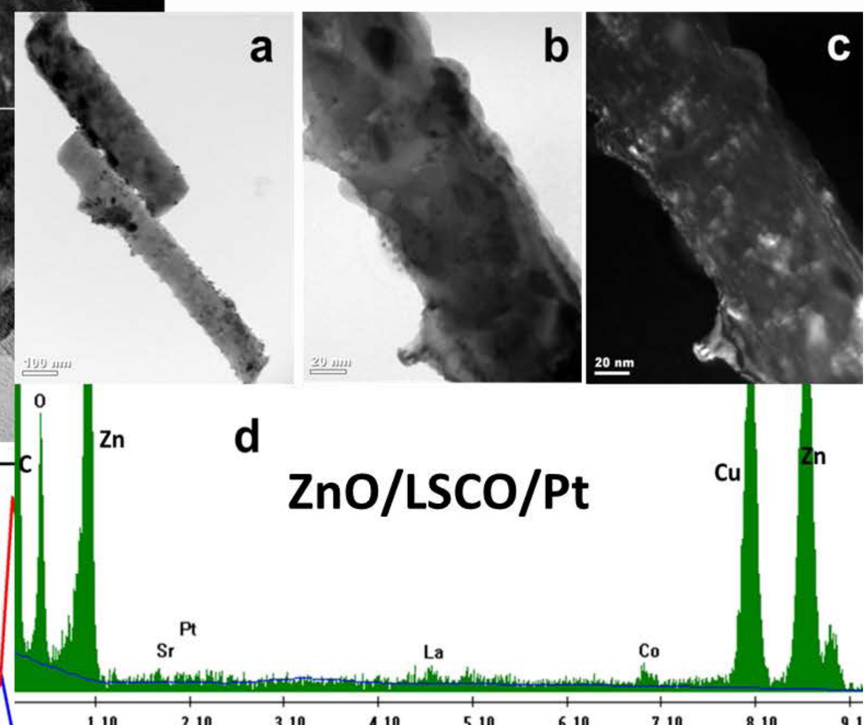
Ren, Gao et al., *Angew. Chem. Int. Ed.*, **2014** , 53(28), 7223–7227.
Guo, Ren, Gao et al., *Nano Energy*, **2013,** 2, 873-881.
Ren, Gao et al., *J. Mater. Chem. A.*, **2013** , 1, 9897-9906 .

Metal Oxide Nano-array based Catalysts

- Solution or vapor phase deposition of the secondary and tertiary components such as noble metal and perovskite nanoparticles.

LSCO: $(La,Sr)CoO_3$





Guo, et al., *Nano Energy*, **2013**.

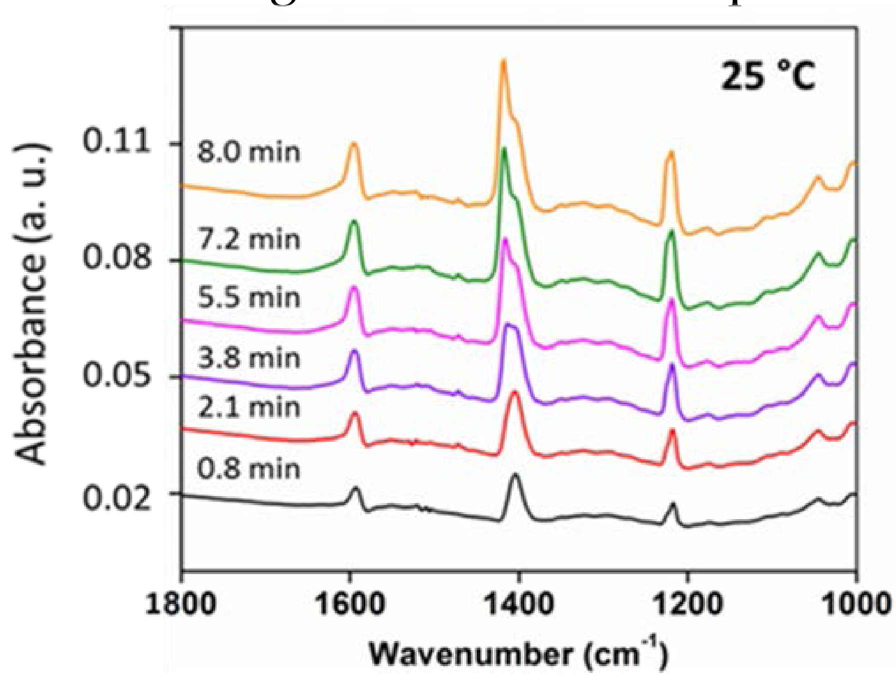
Project Milestones

- **FY15 Quarterly Milestones:**
  - Q1: Synthesize metal oxide nano-array samples for decoration of perovskites
    - complete
  - Q2: Synthesize metal oxide/perovskite nano-array samples for catalytic testing
    - complete
  - Q3: Synthesize metal oxide/perovskite/metal nano-array samples for catalytic testing
    - on track
  - Q4: Characterize structural characteristics of nano-array catalysts in correlation with the catalytic testing performance
    - on track

Collaborations

- Oak Ridge National Laboratory: In-situ spectroscopy characterization of nano-array catalysts with Dr. Zili Wu through Center for Nanophase Materials Science.

  - ❖ Doped Co_3O_4 catalyst for low temperature propane oxidation.
  - ❖ Controlled Ni doping enhanced reaction kinetics and catalytic activity.
  - ❖ A redox reaction mechanism revealed by *in situ* spectroscopy.
  - ❖ Declined thermal stability with Ni concentration due to NiO segregation.



Ren, Wu, Gao, et al., *Appl. Catalysis B*, 2015.

- Brookhaven National Laboratory: metal oxide and metal loading study, and fine structure and chemical analysis of nano-array catalysts with Chang-Yong Nam through Center for Functional Nanomaterials.

Accomplishments

(Project period: 10/1/2014-03/31/2015)

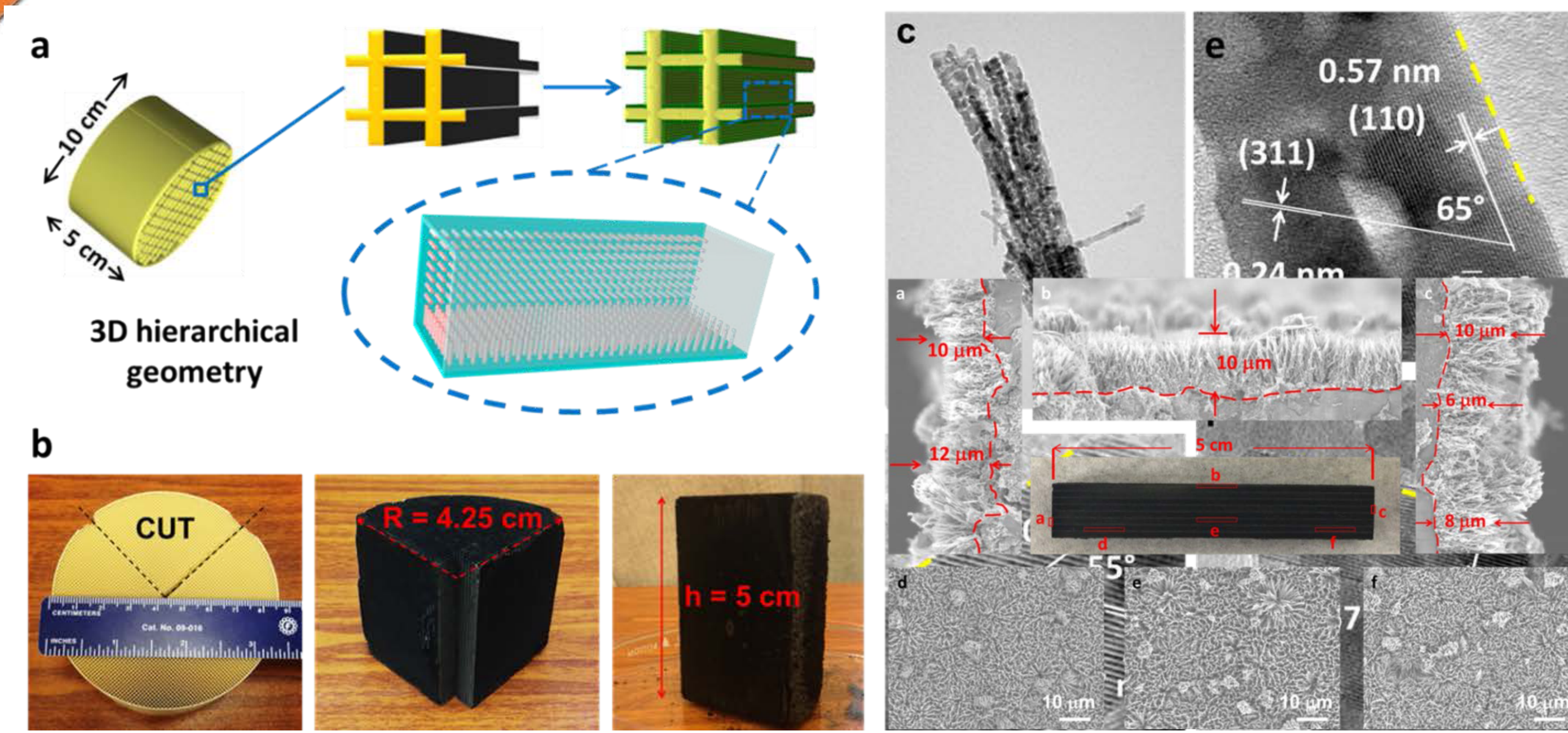
1) Synthesis, characterization and testing of PGM free Co_3O_4 based nano-array based monolithic catalysts.

2) Synthesis, characterization and testing of PGM free MnO_2 based nano-array based monolithic catalysts.

3) Synthesis, characterization and testing of perovskite and Pt nanoparticles loaded metal oxide nano-array catalysts.

4) Formulation and initial testing of promising nano-array based monolithic catalysts with low temperature catalytic oxidation performance toward CO and HCs oxidation.

PGM-free Nano-array Catalysts:
Spinel $M_xCo_{3-x}O_4$ (M=Co, Ni and Zn)

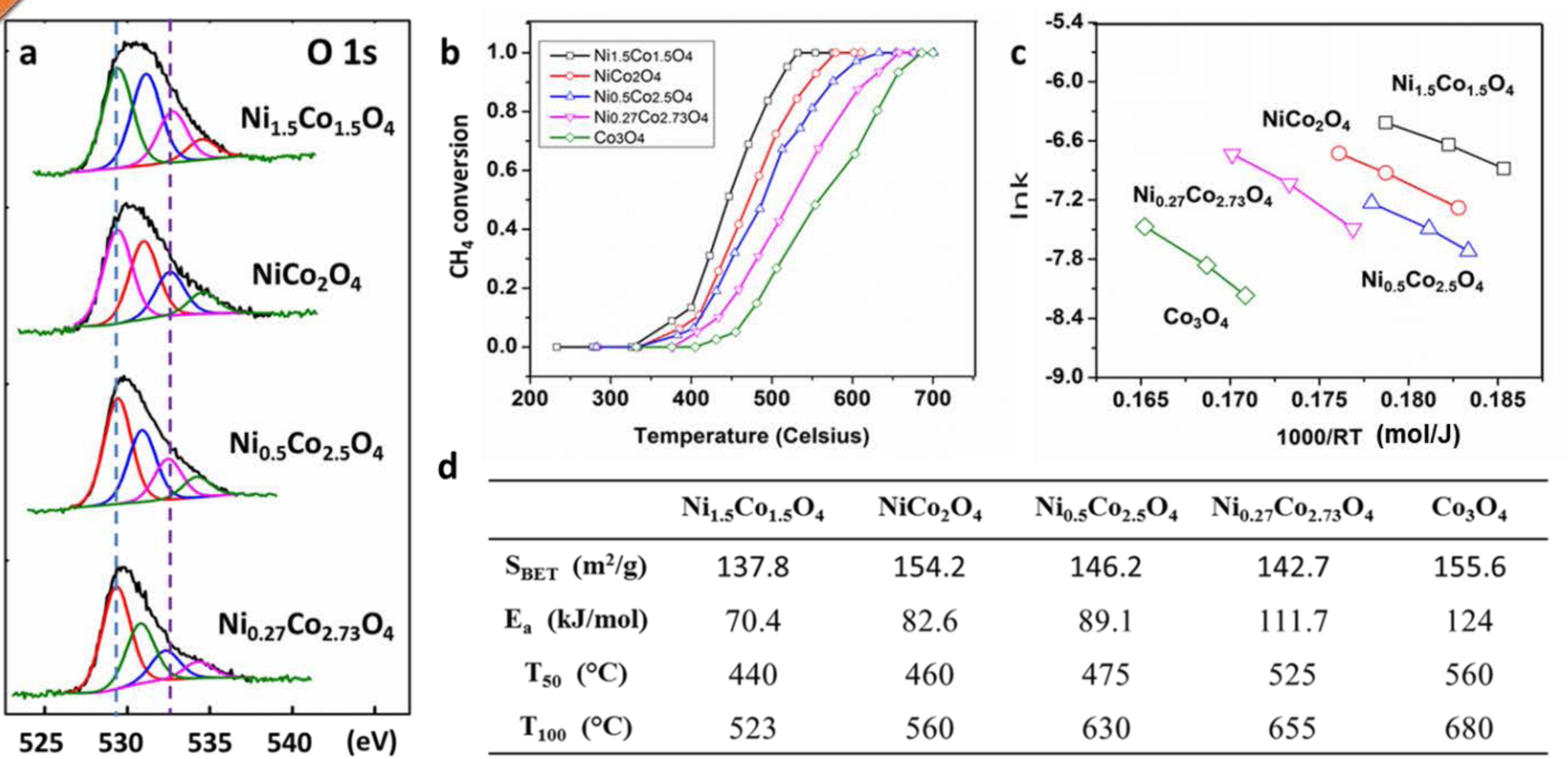


a) Monolithic integration of nano-arrays on commercialized honeycomb supports; b) Photographs of a piece of monolithic nano-arrays catalyst; c) TEM characterization of the Co_3O_4 nanorrays; HRTEM investigation of d) Co_3O_4, e) $Ni_{0.5}Co_{2.5}O_4$ and f) $Zn_{0.5}Co_{2.5}O_4$ nano-arrays.

Ren, Gao, Suib, et al., *Angew. Chem. Int. Ed.*, 2014.

PGM-free Co_3O_4 based Nano-array Catalysts:

Low temperature HC oxidation tunability



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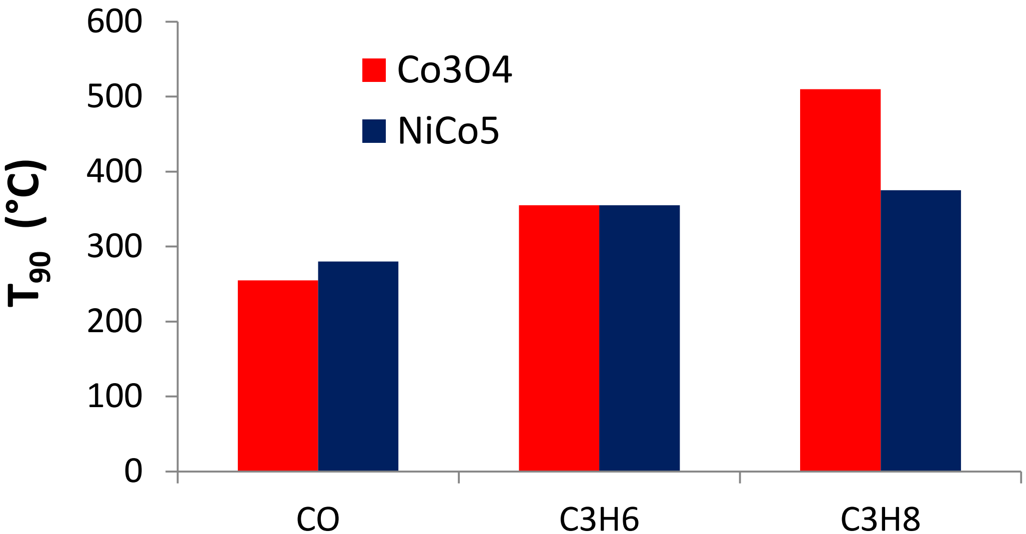
	$Ni_{1.5}Co_{1.5}O_4$	$NiCo_2O_4$	$Ni_{0.5}Co_{2.5}O_4$	$Ni_{0.27}Co_{2.73}O_4$	Co_3O_4
S_{BET} (m^2/g)	137.8	154.2	146.2	142.7	155.6
E_a (kJ/mol)	70.4	82.6	89.1	111.7	124
T_{50} (°C)	440	460	475	525	560
T_{100} (°C)	523	560	630	655	680

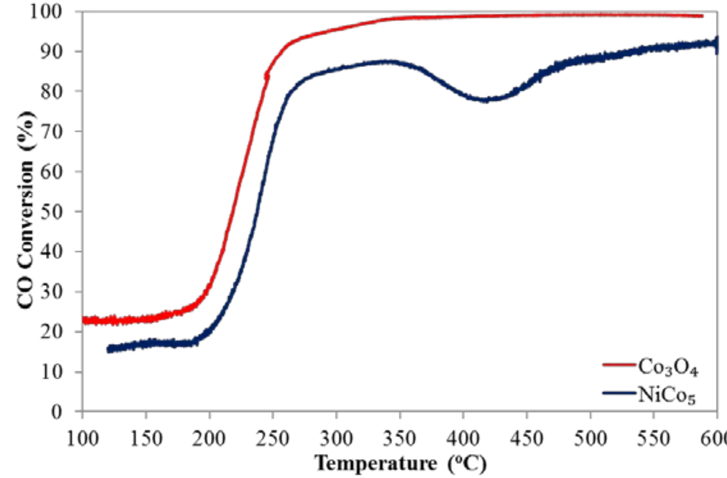
a) XPS spectra of $Ni_xCo_{3-x}O_4$ with different Ni/Co ratios; b) enhanced methane combustion with higher Ni concentration; c) Arrhenius plots of $Ni_xCo_{3-x}O_4$ for methane combustion; d) Summary of surface area, apparent activation energy and characteristic reaction temperatures of $Ni_xCo_{3-x}O_4$.

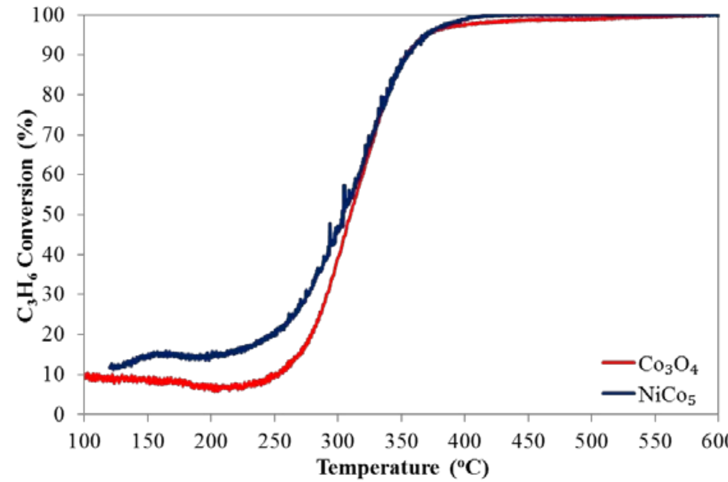
Ren, Gao, Suib, et al., *Angew. Chem. Int. Ed.*, 2014.

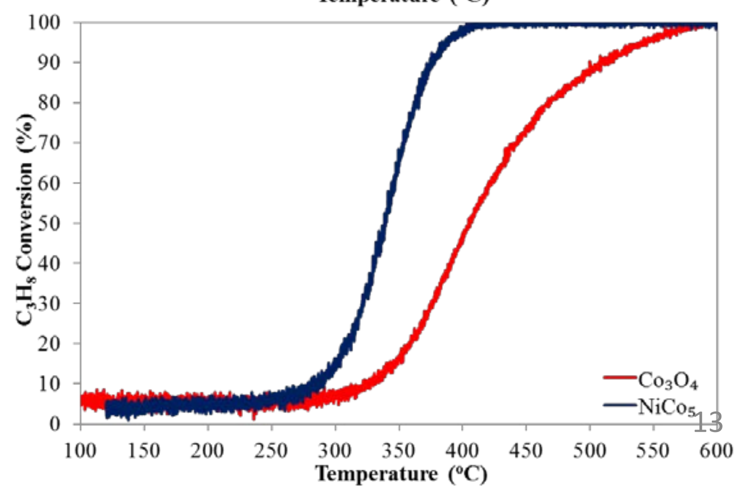
Oxidation Behavior of $NiCo_5$ and Co_3O_4 Catalysts

- Ni-doped Co_3O_4 ($NiCo_5$) and Co_3O_4 nano-array catalysts illustrate a range of activities
  - $NiCo_5$ catalyst better at C_3H_8
  - Co_3O_4 catalyst better at CO and NO to NO_2
- Under conditions analyzed neither meets the goal of 90% conversion at 150°C
  - …but no PGM and room for improvement

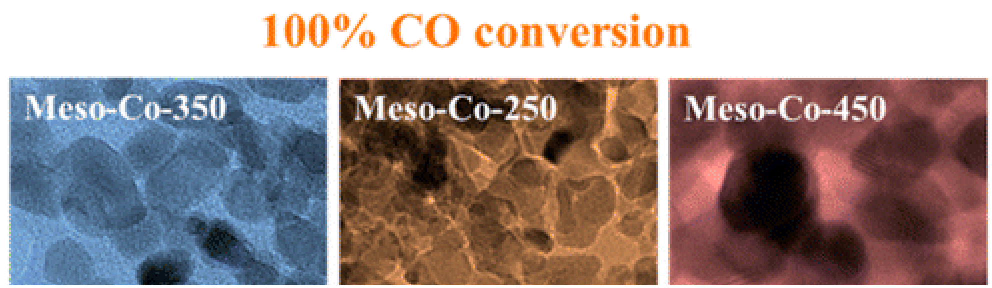




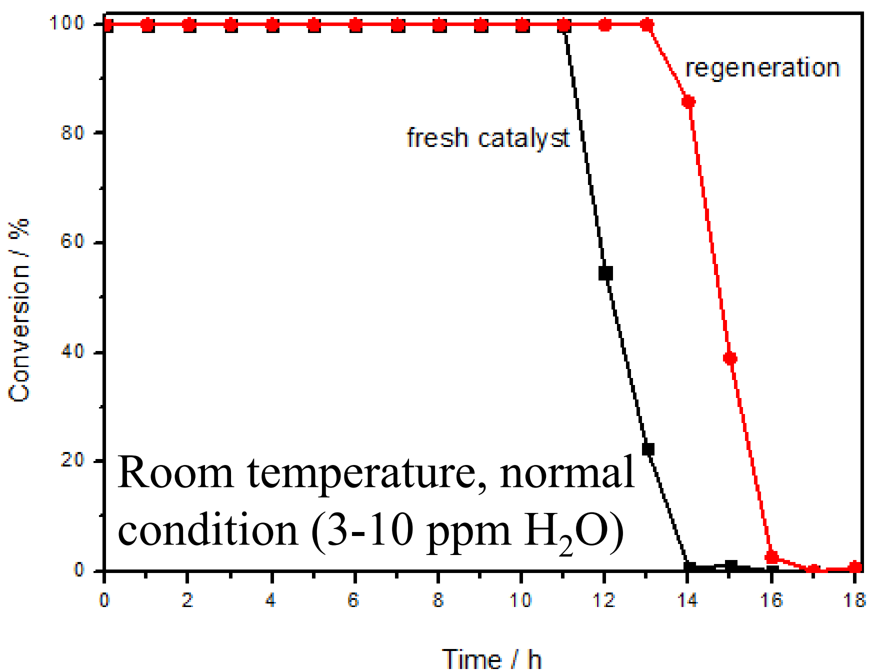


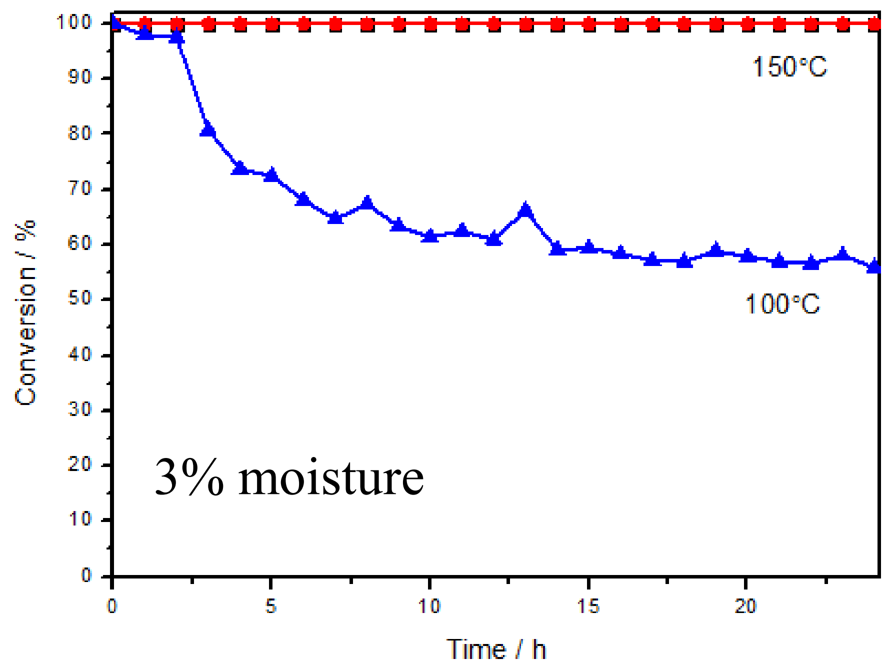


Low Temperature CO Oxidation of Mesoporous Co_3O_4 Nanoparticles



inverse surfactant micelle synthesis method

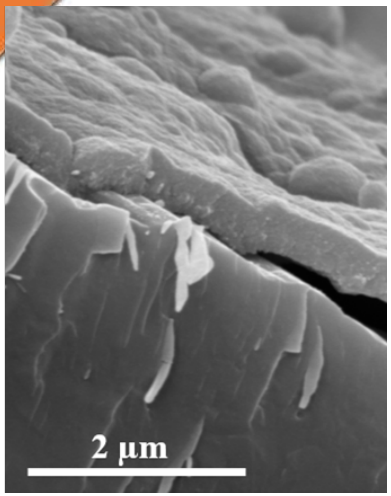


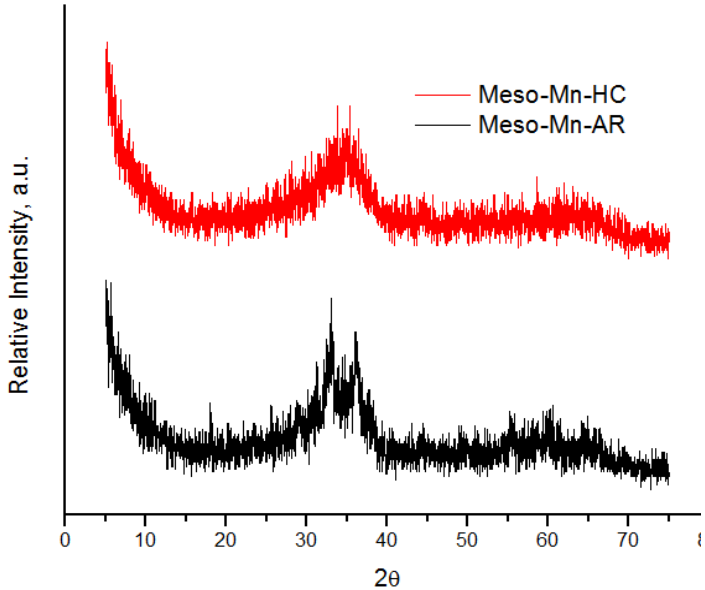


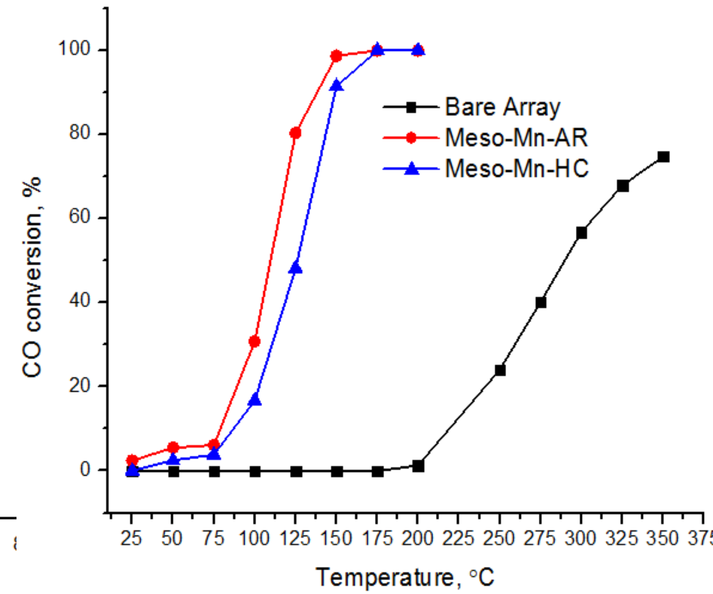
- Low temperature CO oxidation performance of mesoporous Co_3O_4 nanoparticles at normal and moisture condition.

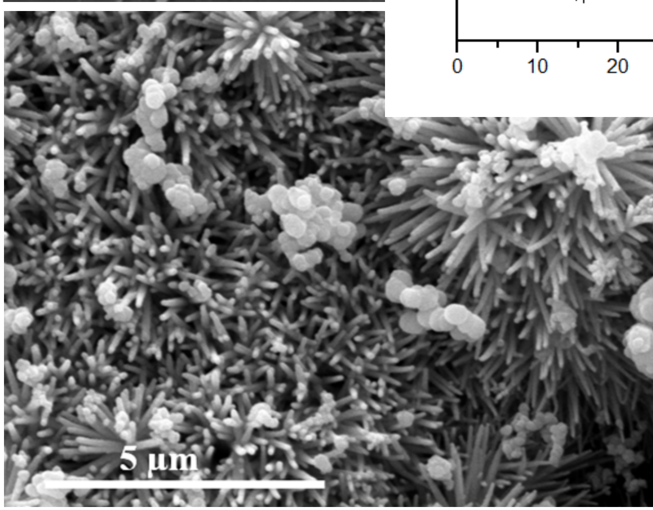
Song, Suib, et al., *Chem. Mater.*, 2014.

Low Temperature CO Oxidation of Mesoporous MnO_2 loaded Nano-arrays









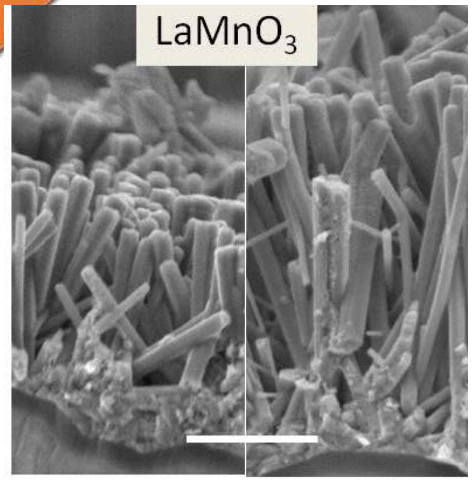
Material	Loading Ratio	Mass loading	T_{50}
Meso-Mn-HC	~ 8%	~ 9 mg	126 °C
Meso-Mn-AR	~ 17%	~ 18 mg	110 °C
Bare array	--	--	290 °C

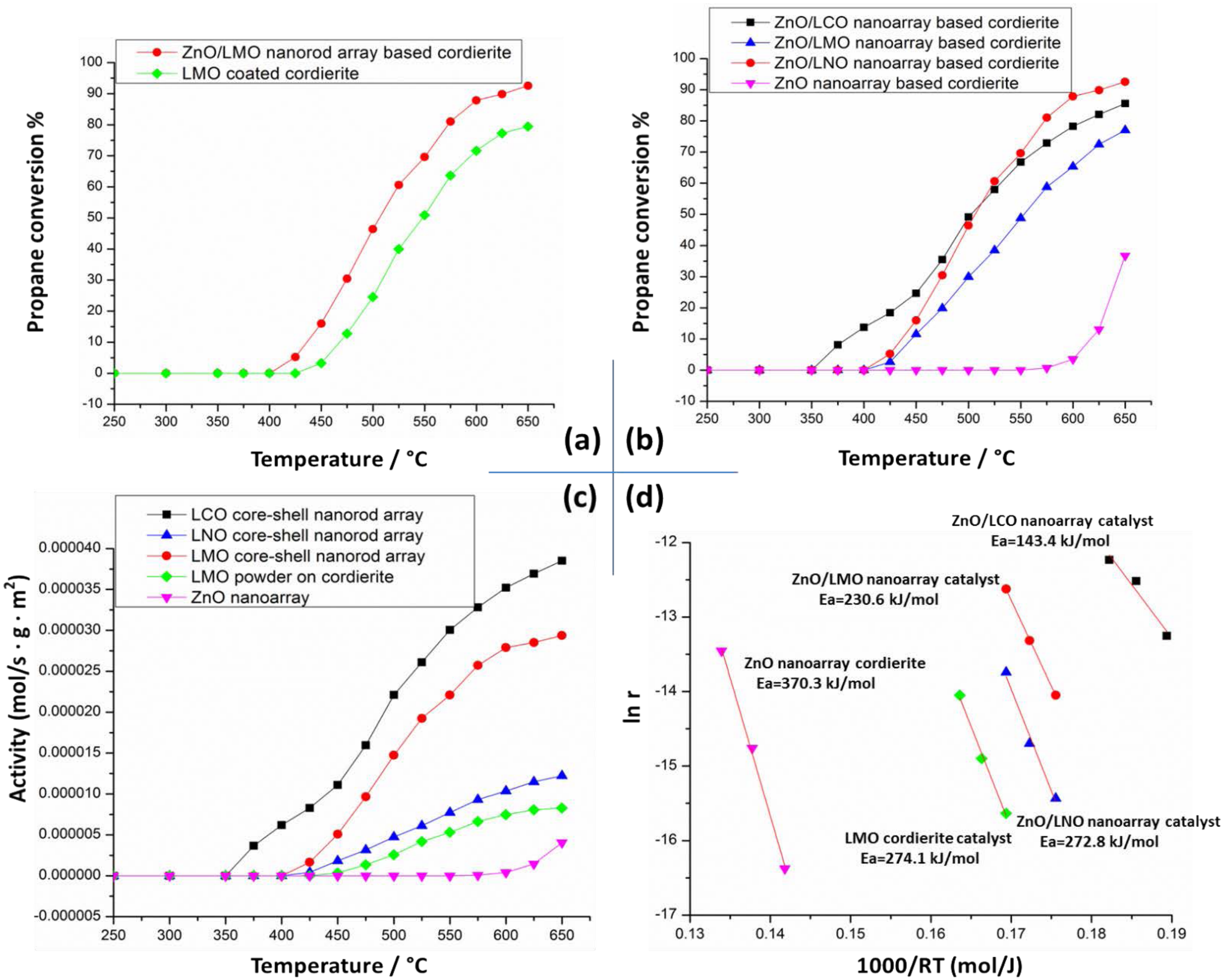
- Low temperature CO oxidation performance of mesoporous MnO_2 decorated MnO_2 nano-arrays at normal condition

Song, Suib, et al., *unpublished,* 2015.

Perovskite loaded Nano-arrays:

Propane Oxidation

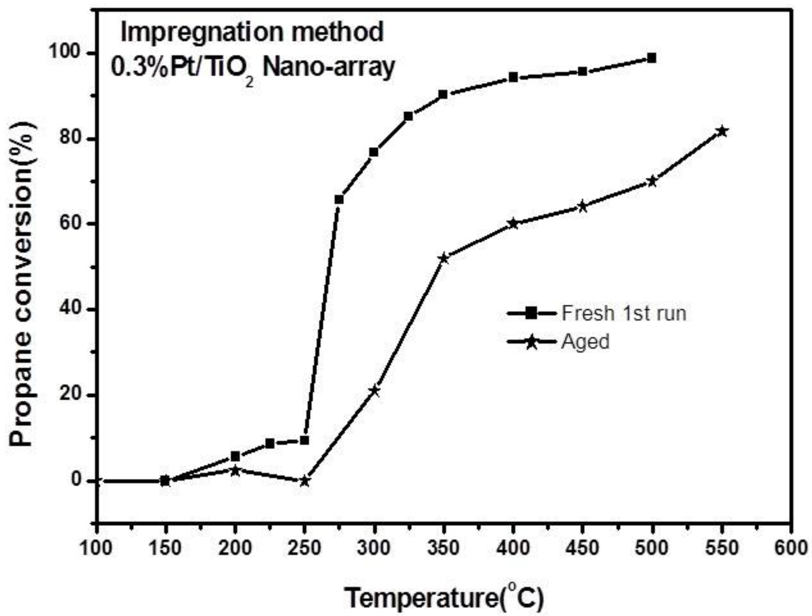


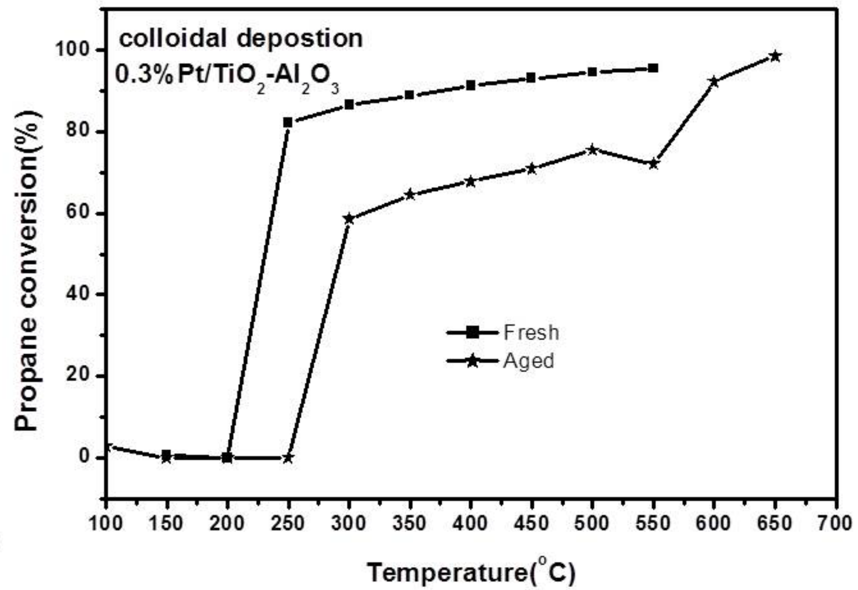


- Interface/loading effects: 25°C lower light-off temperature than wash-coated perovskite catalys (LMO loading, 4.3mg);
- Composition effect: $ZnO/LaBO_3$ nano-arrays with catalytic activity sequence of $LaCoO_3$ > $LaMnO_3$ > La_2NiO_4 at the initial stage of catalytic reaction

Wang, Guo, Ren, Song, Suib and Gao, *Catalysis Today*, 2015.

Pt/TiO_2 based Nano-array Catalysts: *Propane Oxidation*

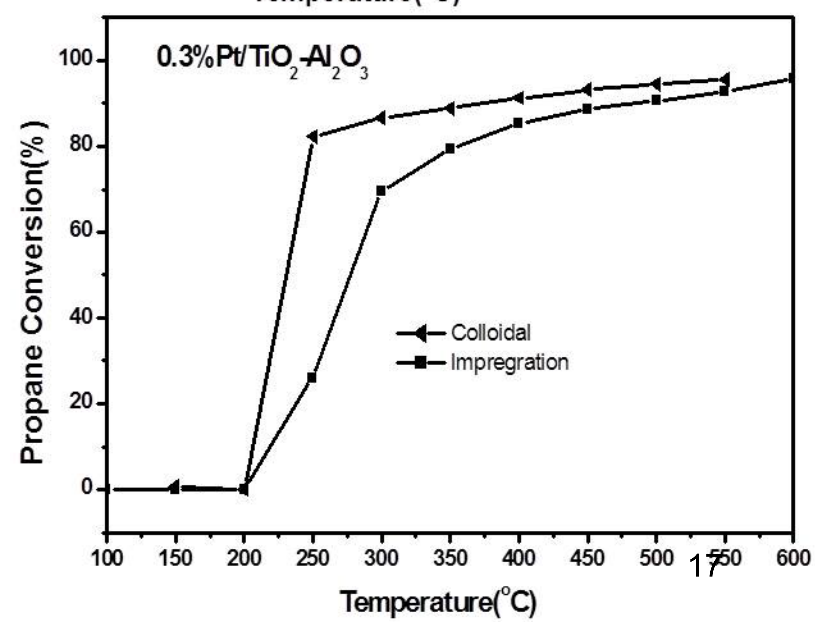




* Hydrothermal aging: 10% H_2O vapor 800°C,10hours

- 0.3 wt.% Pt loaded TiO_2 and TiO_2-Al_2O_3 nano-array monoliths: ~ 80% C_3H_8 conversion at ~250°C. SV: 36,000 h^{-1}
- Colloidal deposition better than impregnation in catalyst performance.
- Hydrothermal aging degrades catalytic performance, with Pt/TiO_2-Al_2O_3 better sustained.

Hoang, Guo, Gao, et al., *unpublished,* 2015.



Future work

1) Formulation of selective metal oxide nano-array catalysts with good catalytic oxidation performance at 150 ^{o}C or lower.

2) Optimized loading of the noble metal and perovskite nanoparticles on selective nano-array catalysts.

3) Evaluation of oxidation behavior of nano-array catalysts over CO and HCs oxidation under simulated exhaust atmosphere.

4) Assembly of large scale and selective nano-array catalysts for engine testing in FY 16.

Acknowledgements

- Postdoc: Drs. Y. Guo, S. Hoang, W. Tang

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- Collaborators: Drs. Z. Wu, S. Overbury, J. Parks (ORNL), Dr. C. Nam, D. Su, H. Chen (BNL)
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